View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by ScholarWorks@UMass Amherst

Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 14 Article 27

January 2010

Characterization Of A VOC Plume Migrating From Fractured Shale Into A Karst Limestone Aquifer

Paul G. Landry

Bryan L. Hoke

Paul R. Stone III

Follow this and additional works at: https://scholarworks.umass.edu/soilsproceedings

Recommended Citation

Landry, Paul G.; Hoke, Bryan L.; and Stone, Paul R. III (2010) "Characterization Of A VOC Plume Migrating From Fractured Shale Into A Karst Limestone Aquifer," *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 14 , Article 27.

Available at: https://scholarworks.umass.edu/soilsproceedings/vol14/iss1/27

This Conference Proceeding is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy by an authorized editor of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Chapter 26

CHARACTERIZATION OF A VOC PLUME MIGRATING FROM FRACTURED SHALE INTO A KARST LIMESTONE AQUIFER

Paul G. Landry, P.G.[1§], Bryan L. Hoke[2], Paul R. Stone, III[3]

[1]*1400 Weston Way, West Chester, PA, United States, 19380,* [2]*1 Overcash Avenue, Chambersburg, PA, United States, 17201,* [3]*1 Overcash Avenue, Building 14, Chambersburg, PA, United States, 17201.*

ABSTRACT

Delineation of the non-aqueous phase liquid (NAPL) source zone in the vicinity of an oil burn pit (OBP) at Letterkenny Army Depot (LEAD) revealed the presence of source material on both sides of a nearby groundwater divide resulting in a bilobate plume. While the northern lobe of the plume migrating from the OBP had been well defined, the southern lobe of the plume had been previously undetected. An investigation was initiated to determine whether the southern lobe of the plume had reached the Pinola Fault (900 ft downgradient), the formation contact between the Martinsburg Shale and the St. Paul Limestone, and if so, what impacts the plume was having on groundwater/surface water quality in the limestone aquifer. Dye tracing and aquifer tests had shown significant differences in groundwater velocities between the two rock types (i.e., ft/year in the shale versus >2,000 ft/day in the limestone).

The migration pathway and extent of the plume moving south was mapped using geoprobe/soil gas sampling, and verified by well installations. The soil gas results correlated extremely well with the travel path and extent of the contaminated groundwater within the shale. The strong soil gas/groundwater quality correlation was attributed to both shallow groundwater and slow velocities within the shale, which allowed for the accumulation of soil gas vapors. In this manner, the plume was effectively mapped down to the fault contact and the plume entry location into the limestone was identified. Volatile organic compound (VOC) sampling results to date indicate minimal impact from the plume on limestone groundwater quality. Rapid groundwater velocities and extensive karst development result in significant declines in contaminant levels a short distance from the fault. Dye tracing results from wells at the plume entry location and at numerous downgradient wells throughout the limestone basin appear to substantiate these findings.

Keywords: Non-aqueous phase liquids; karst; dye tracing; soil gas

§ Corresponding Author: Paul G. Landry, P.G., 1400 Weston Way, West Chester, PA, 19380, 610-701-7273, P.Landry@WestonSolutions.com

1. INTRODUCTION

The Letterkenny Army Depot (LEAD) is situated on the western side of the Cumberland Valley, just north of Chambersburg, Pennsylvania, in the Valley and Ridge physiographic province. The bedrock underlying LEAD is composed of complexly folded and faulted Ordovician limestones and shales that were deformed during the tectonic events that formed the Appalachian Mountains (Becher and Taylor, 1982). The OBP at LEAD is located approximately 300 feet east of the intersection of Georgia Avenue and Scale House Road (Figure 1), and is situated near the crest of a hill where 3 groundwater drainage divides converge. Underlying the OBP is the Martinsburg Shale Formation, a fissile to massive shale containing thin interbeds of siltstones, sandstones, and greywackes. The Martinsburg shale typically forms small ridges or upland areas in the valley as it is more resistant to chemical/physical weathering than the local carbonate rocks. Located approximately 900 feet south of the OBP is the Pinola Fault, a reverse thrust fault that forms the contact between the Martinsburg shale and the St. Paul Limestone. The St. Paul Limestone is a micritic, granular limestone that chemically weathers to form extensive karst features such as sinkholes, voids, and losing stream segments throughout the local valleys.

As part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) investigations at LEAD during the 1980s and 1990s, the oil burn pit (OBP) soils were identified by the Army as an area of concern and a potential source of groundwater contamination. The OBP had operated in the 1970s and was used for fire training and the disposal of waste oil and solvents from industrial missions at LEAD. While several time-critical removal actions of OBP soils were performed by the Army in the late 1990s, groundwater investigations in the OBP area conducted through 2002 indicated that significant volatile organic compounds (VOCs) were present in the OBP area groundwater. In addition, non-aqueous phase liquids (NAPLs) were present in several OBP wells, with 1,1,1-trichloroethane being the most elevated contaminant of concern. As shown on Figure 1, a VOC contaminant plume was mapped emanating from the OBP toward the north and Meghan Mackenzie Run (MMR). In 2003, the Army initiated an investigation to delineate the extent of NAPL material in the area of the OBP.

2. DELINEATION OF NAPL SOURCE ZONE IN OBP AREA

Due to both the presence of NAPL at the site and the complexities of the fractured bedrock system, the Army began negotiations with EPA Region III for a Technical Impracticability (TI) waiver as a component of the ultimate site remedy in early 2003. As a condition for TI waiver consideration, a thorough delineation of the NAPL source zone at the site was required. In 2003 and 2004, the Army conducted a drilling and sampling program at the site to delineate the lateral and vertical extent of NAPL source material in the OBP area. The program involved the use of real-time field screening methods during drilling such as hydrophobic dye testing of rock and water samples and heated headspace analysis to screen for the presence of NAPL material. As shown on Figure 1, a series of 4 well locations (03-PDO-3 through 03-PDO-6) were proposed for this effort, moving outward from areas of the OBP known to contain NAPL material. Results of this effort indicated that NAPL material associated with the OBP were present in the groundwater south of the PDO OU 4/OU 2 drainage divide. As shown on Figure 2, two shallow monitoring wells (04-PDO-2 and 04-PDO-3) were installed in the northernmost revetment that

contained NAPL material and/or effective solubility concentrations of 1,1,1-TCA indicative of NAPL presence (ranging between 50 mg/L to 90 mg/L).

3. DISCOVERY OF CONTAMINATED SEEP AREA DURING TBR/OTL INVESTIGATIONS

Concurrent with the NAPL delineation program in the OBP area, the Army had also initiated investigation of the Transfer Burning Revetments (TBR) and Open Trench Landfill (OTL) sites located south of the OBP. The initial investigation at these sites included a surface geophysical survey, followed by sampling of test trenches, soil borings, and local drainage ways. Analytical results from these sampling efforts indicated that there were no apparent sources of VOCs present in the revetment area soils. However, in the drainage swale along the eastern edge of Scale House Road, a seep was discovered that contained 5,600 µg/L of 1,1,1-TCA. Subsequent re-sampling of this seep and the adjacent piezometer indicated consistent 1,1,1-TCA levels ranging from 4,000 to 4,200 µg/L (see Figure 2).

A follow-up investigation to evaluate the source and character of the seep contamination was performed that included a geophysical survey of the swale and the immediate vicinity upgradient of the seep in both the TBR and OTL areas. An extensive soil boring and sampling program conducted following the geophysics revealed that the source of the seep contamination appeared to be in the bedrock groundwater, and not in the soils upgradient from the seep. The maximum detected 1,1,1-TCA concentration in the soil samples was 240 µg/kg, whereas the aqueous samples from the seep contained 1,1,1-TCA levels in excess of 4,000 µg/L.

4. TWO-PHASED SOIL GAS SAMPLING PROGRAM PROVIDES USEFUL GROUNDWATER DATA

To further evaluate the source of the seep contamination and to potentially map the migration pathway of groundwater contamination moving farther downgradient, an extensive, 2-phase soil gas/sampling program was performed in 2003 and 2004 at the site. The soil gas/sampling program was performed using Geoprobe® drilling methods, whereby soil gas samples were collected at bedrock refusal and run through field calibrated flame ionization detectors (FIDs). The FIDs were selected due to their high sensitivity for 1,1,1-TCA (estimated >95% response factor). For quality control, approximately 20% of all soil gas samples were retained in tedlar bags and sent for fixed laboratory analysis of VOCs. As shown on Figure 3, soil gas samples were collected from approximately 56 locations during Phase 1, and 67 locations during Phase 2. The Phase 2 soil gas locations are distinguished from the Phase 1 locations by the soil gas lines shown on Figure 3.

Produced by The Berkeley Electronic Press, 2009

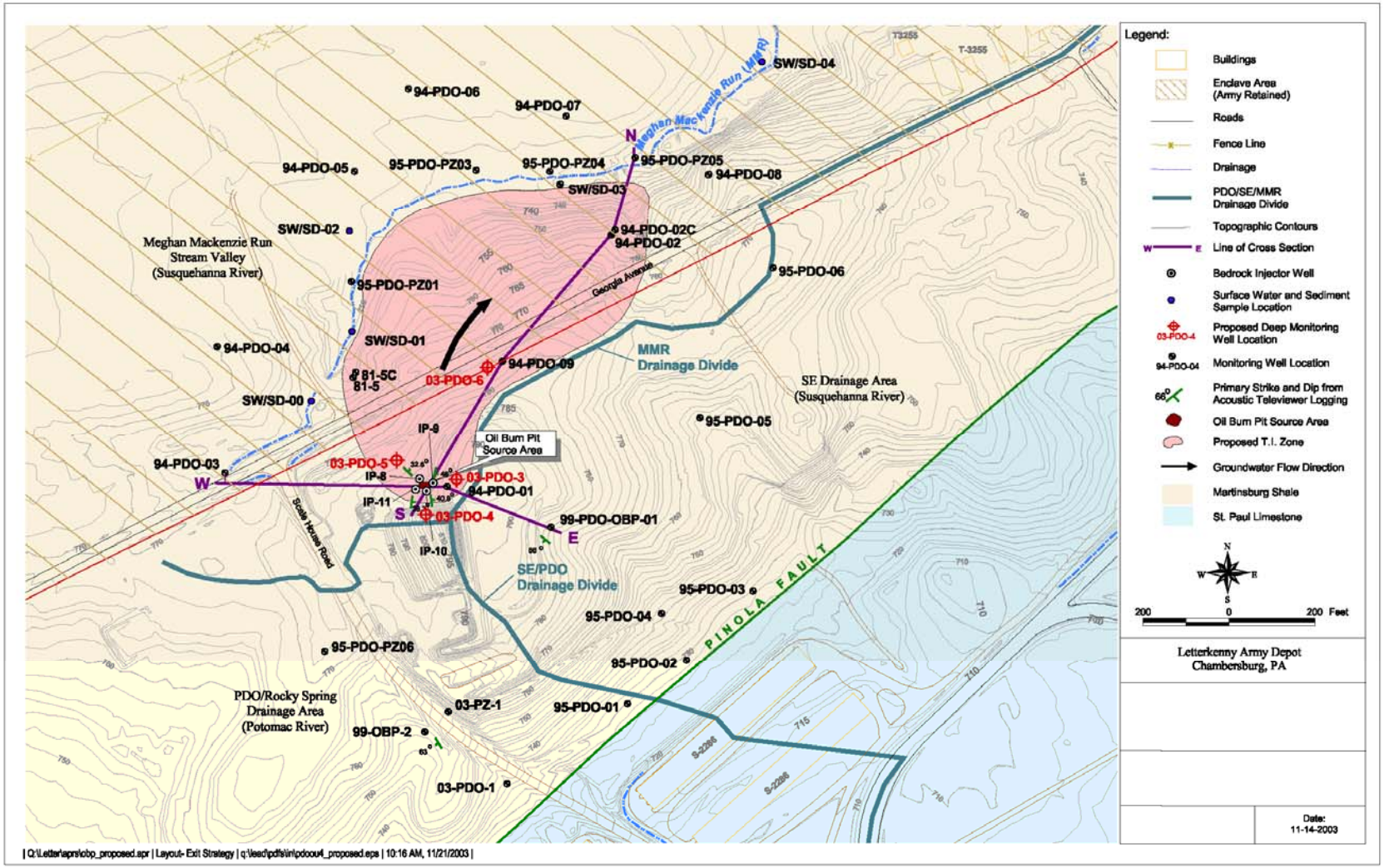

Figure 1. Geologic Map of the Oil Burn Pit Area Showing the Contaminant Plume Prior to the NAPL Delineation Program

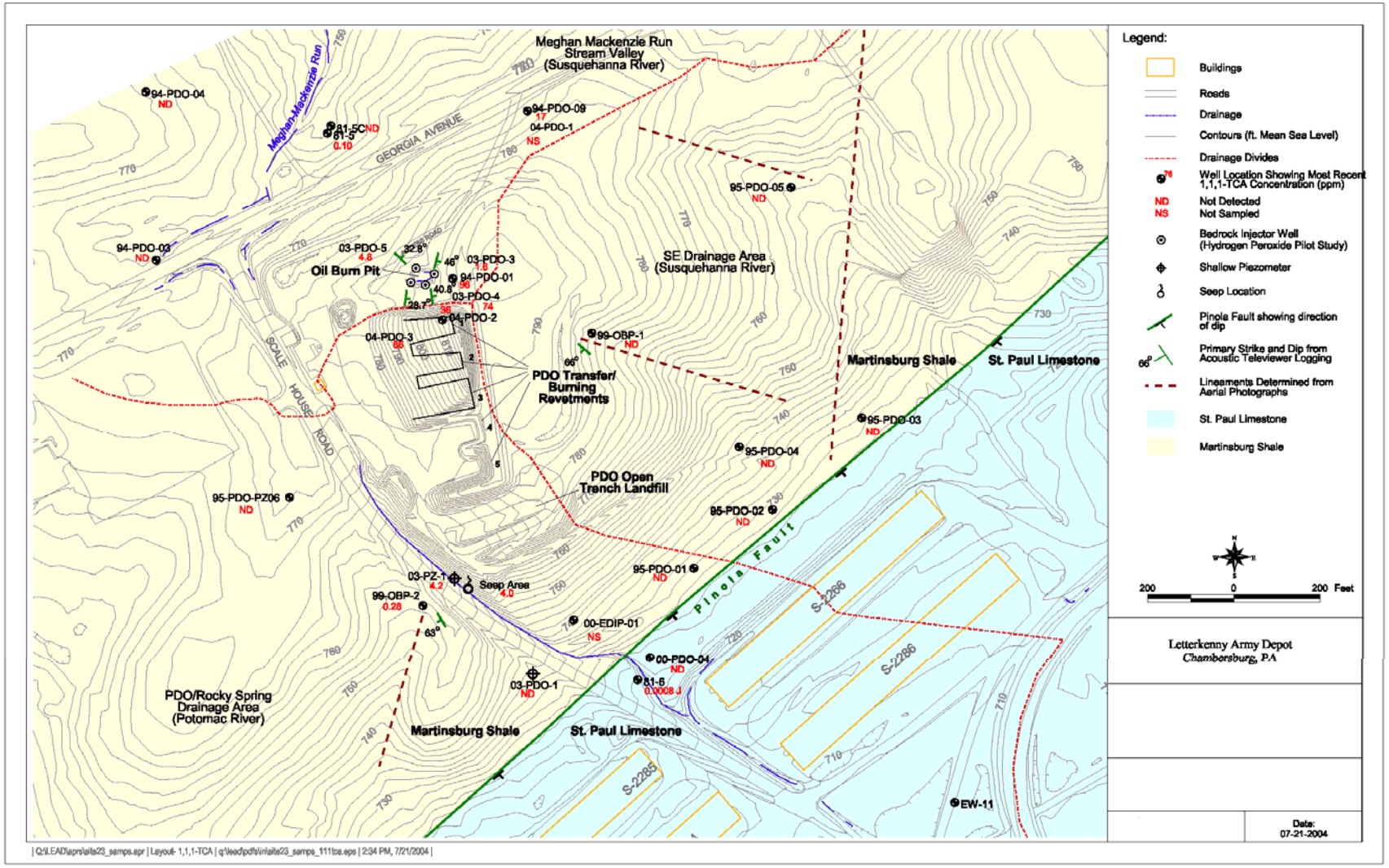

Figure 2. Recent/Historical 1,1,1-TCA Groundwater Concentrations at the Oil Burn Pit, Transfer Burning Revetments and Open Trench Landfill Area Following NAPL Delineation Program

Soil gas concentrations exceeding 100,000 µg/L were used to infer the presence of elevated 1,1,1-TCA concentrations emanating from the groundwater at each location (see highlighted values on Figure 3). The results of the soil gas program indicated that elevated concentrations (>100,000 µg/L) of 1,1,1-TCA appeared to be volatilizing off the bedrock groundwater and a source of VOCs appeared to be present in the upper TBR area. These results verified the findings of the NAPL delineation program, which showed source material to be present just south of the MMR/PDO groundwater divide in wells 04-PDO-2 and 04-PDO-3 (Figure 2). As shown on Figure 3, elevated soil gas readings were mapped and traced from the uppermost revetment, down along Scale House Road in the vicinity of the seep area and well 99-OBP-2, and further toward the south-southwest and the Pinola Fault area.

The strong correlation observed between soil gas results and contaminant concentrations in groundwater were attributed to the combination of shallow groundwater levels (<20 ft), shallow depth to bedrock (15-20 ft), low seasonal variations in groundwater levels (5-7 ft) and the slow groundwater velocities (<1 ft/day) observed in the Martinsburg Shale at LEAD.

5. MONITORING WELL NETWORK VERIFIES THE MIGRATION PATHWAY OF THE PLUME

The soil gas results were used to sequentially cite the locations for groundwater monitoring wells and piezometers down to the Pinola Fault area between 2003 and 2006. As shown on Figure 4, the migration pathway of the groundwater plume was mapped down to its entry location in a persistently wet area adjacent to the Pinola Fault. Limestone well 04-PDO-11 contained 1,1,1-TCA levels ranging from 750 to 1,000 µg/L, by far the most impacted limestone well in the PDO area of LEAD at the time. Subsequent well installations in this area on both sides of the of the Pinola Fault suggest that the plume is migrating primarily in the shallow, fractured bedrock zone within the shale, crossing the fault into the St. Paul Limestone and dispersing both laterally and vertically within the limestone. As shown on the hydrogeologic cross-section of the Pinola Fault area (Figure 5), the most elevated 1,1,1-TCA concentrations are found in the shallow bedrock wells on either side of the fault (06-PDO-4, 06-PDO-5, and 05-PZ-4).

Additional limestone wells (05-PDO-2 through 05-PDO-4) installed downgradient from this plume entry location at the fault encountered significant karst solution features during drilling/installation (i.e., a 20-foot aperture void was encountered in monitoring well 05-PDO-2). In addition, concentrations of 1,1,1-TCA, and all VOCs, dropped significantly from the Pinola Fault area to these 3 wells (see Figure 4). Farther downgradient of these wells, concentrations of 1,1,1-TCA in groundwater remain low throughout the limestone basin at LEAD down to the convergent surface water discharge at Rocky Spring. In fact, VOC levels throughout the PDO area at LEAD have been shown to be on a steady decline since the late 1980s. The Army theorizes that while the newly discovered plume has likely been discharging slowly from the shale into the limestone for many years, the extensive karst development in the St. Paul and Chambersburg limestones have a pronounced attenuating effect on the plume. In a series of dye trace studies completed by the Army in 1999-2000, groundwater velocities observed in the

limestone aquifer in this area of LEAD were shown to range from 1,080 ft/day to >4,800 ft/day (WESTON, 2004). To further verify the fate and transport of the newly discovered plume that is discharging across the Pinola Fault from the shale into the limestone, the Army initiated a dye tracing program in 2006. The results from Phase I of the Upper PDO dye tracing program are discussed briefly below.

6. UPPER PDO DYE TRACING PROGRAM – PHASE I RESULTS

As shown on the map provided as Figure 6 and Table 1-A, eosine dye was introduced into well 04-PDO-11 at the Pinola Fault on 5 December 2007 in accordance with the procedures detailed in the final technical plan (WESTON, 2006). *Note:* A second dye (sulforhodamine B) was also introduced in another area of the PDO (Pad 5 Landfill) (Table 1-B) to determine the fate and transport of contaminants from a smaller, localized source area, but these results will not be discussed herein. The results of the dye trace from the Pinola Fault area showed that well 04-PDO-11 is in hydraulic communication with 7 of the 11 locations sampled during Phase I. Groundwater velocities ranged from a low of 21.5 ft/day to a high of 3,570 ft/day, indicating that multiple groundwater flow pathways exist in the karst basin. Dye from well 04-PDO-11 reached Rocky Spring House within 3 to 6 days (1,669 to 3570 ft/day), a travel distance of nearly 1.5 miles to the southwest. Conversely, dye from 04-PDO-11 reached nearby downgradient well 05-PDO-2 between 6 and 13 days (21 to 47 ft/day). Results of the dye trace also show well 04-PDO-11 to be in hydraulic communication with well 81-4 (located approximately 2,350 downgradient), with groundwater velocities ranging from 67 to 107 ft/day. The significance of this finding is that well 81-4 was shown to contain elevated concentrations of 1,1,1-TCA in the 1980s (>1,000 µg/L). However, this well now contains less than 3 µg/L of 1,1,1-TCA and contains no VOCs in excess of EPA maximum contaminant levels (MCLs). The overall conclusion from Phase I of the dye study is that the extensive karst development in the limestone aquifer in the PDO area of LEAD results in significant attenuation of contaminant levels discharging across the Pinola Fault from the shale into the limestone. A second phase of the upper PDO dye trace is currently underway to determine the groundwater velocities in the Martinsburg Shale from the OBP source area down to the Pinola Fault. However, while dye was introduced into several well locations within the shale in April 2007, as of March 2008, no positive dye detections have yet been observed. These results further verify the extremely slow travel times within the Martinsburg Shale.

Produced by The Berkeley Electronic Press, 2009

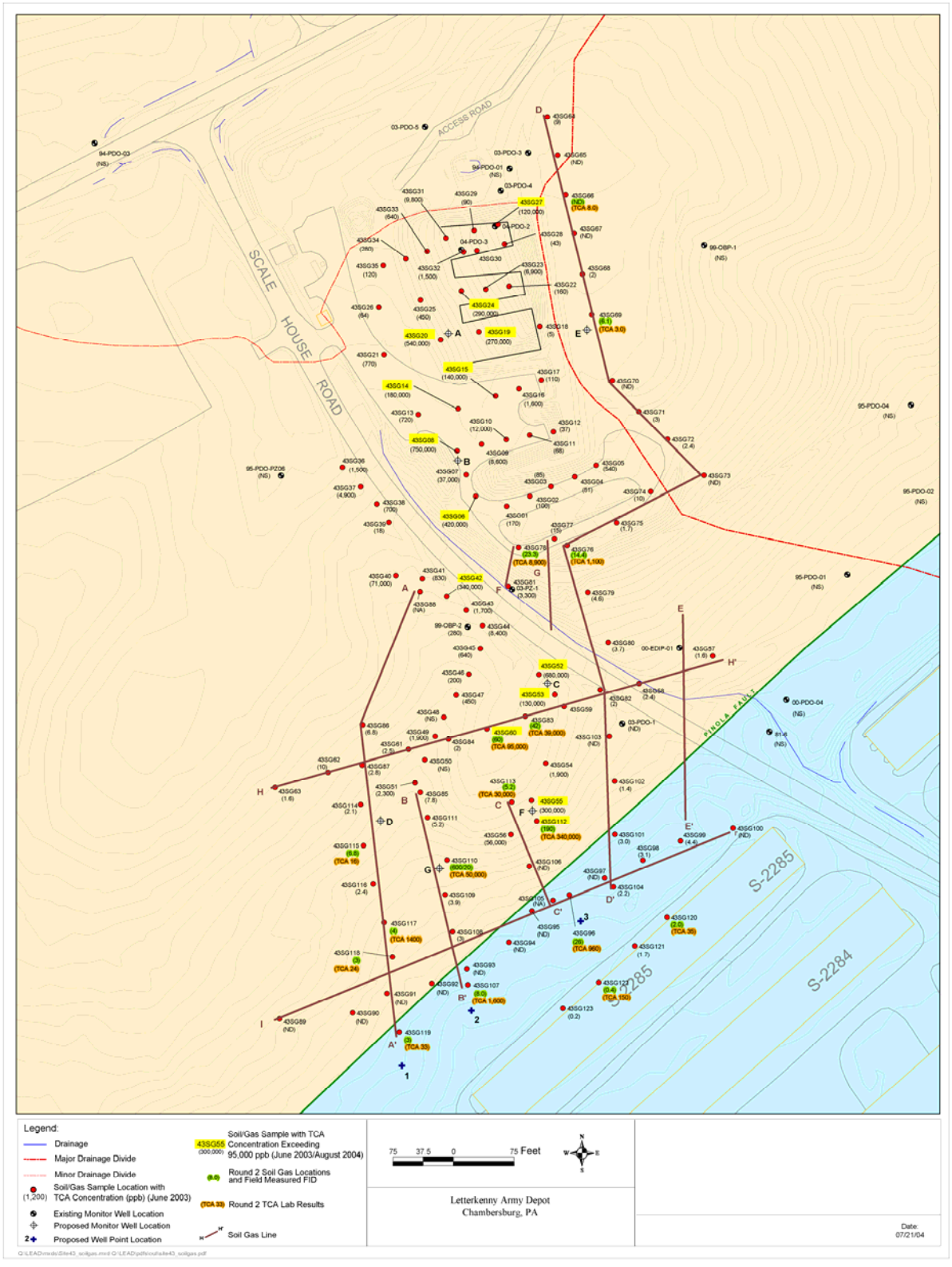

Figure 3. Soil Gas Results and Proposed Monitor Well Locations for Further Delineating the Extent of the OTL/TBR Area Groundwater Plume

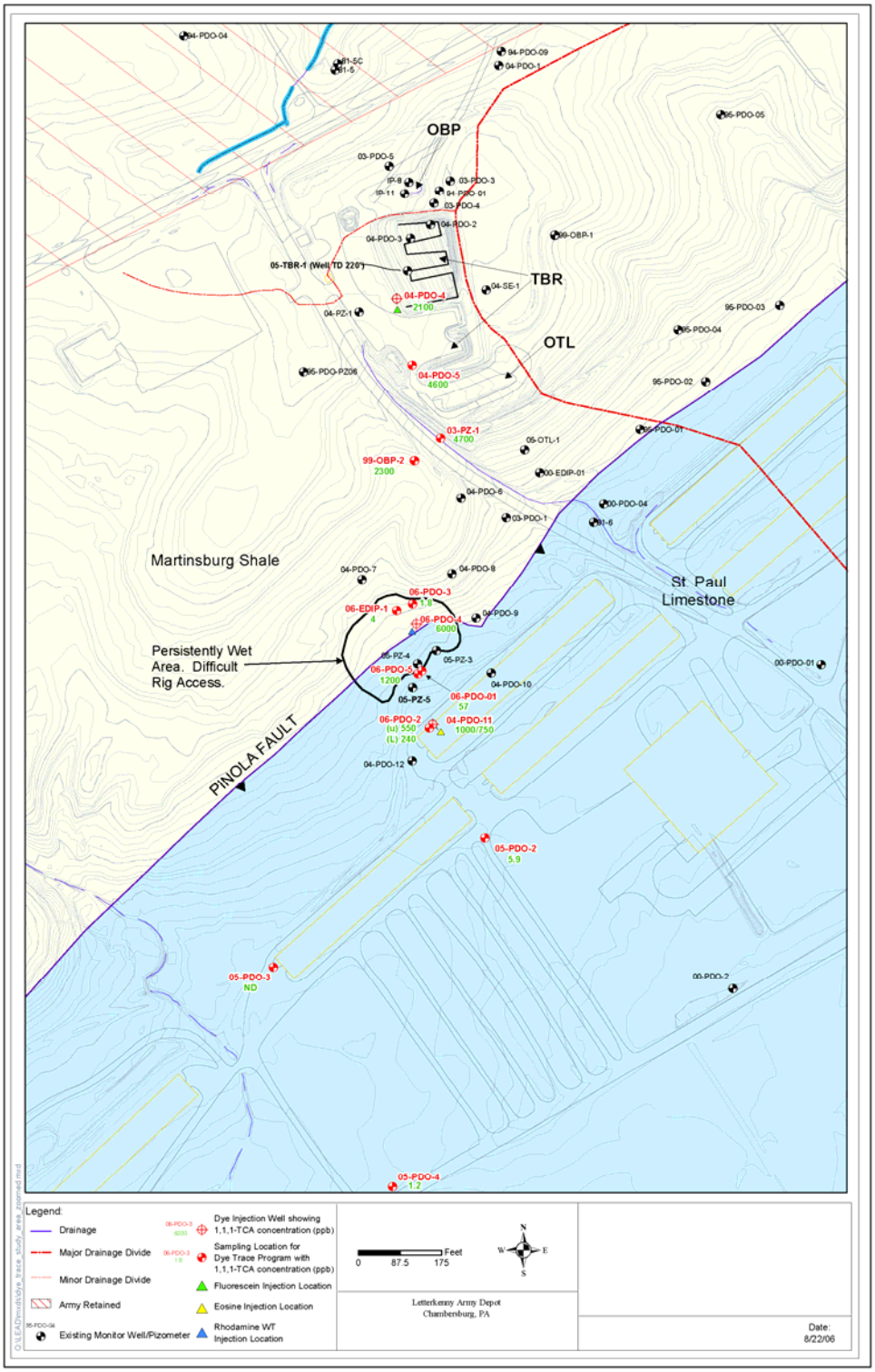

Figure 4. Dye Injection and Sampling Locations in the Upper PDO/Pinola Fault Area Showing Recent 1,1,1-TCA Concentrations

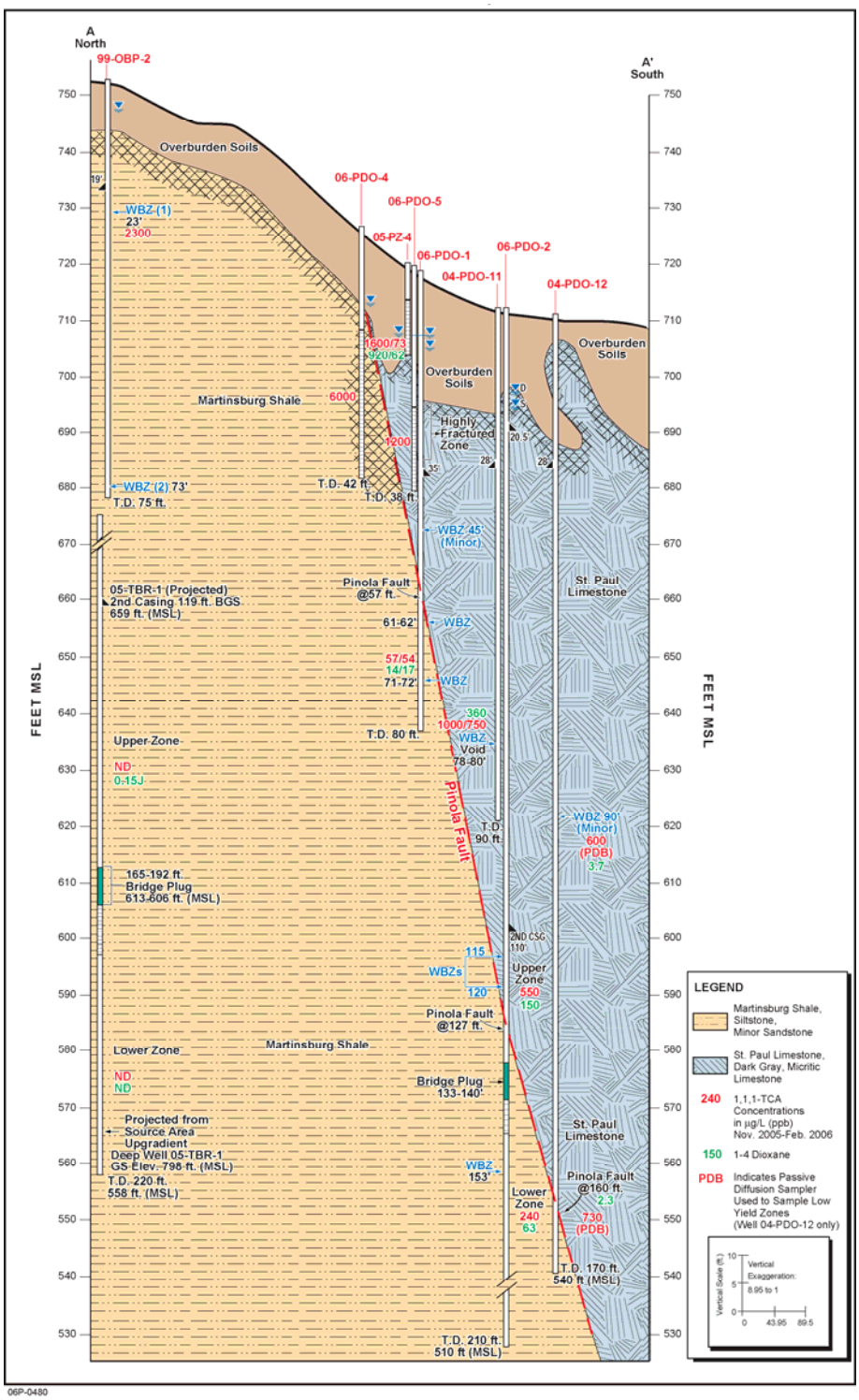

Figure 5. North South Hydrogeologic Cross-Section of the Pinola Fault Area in the Upper PDO

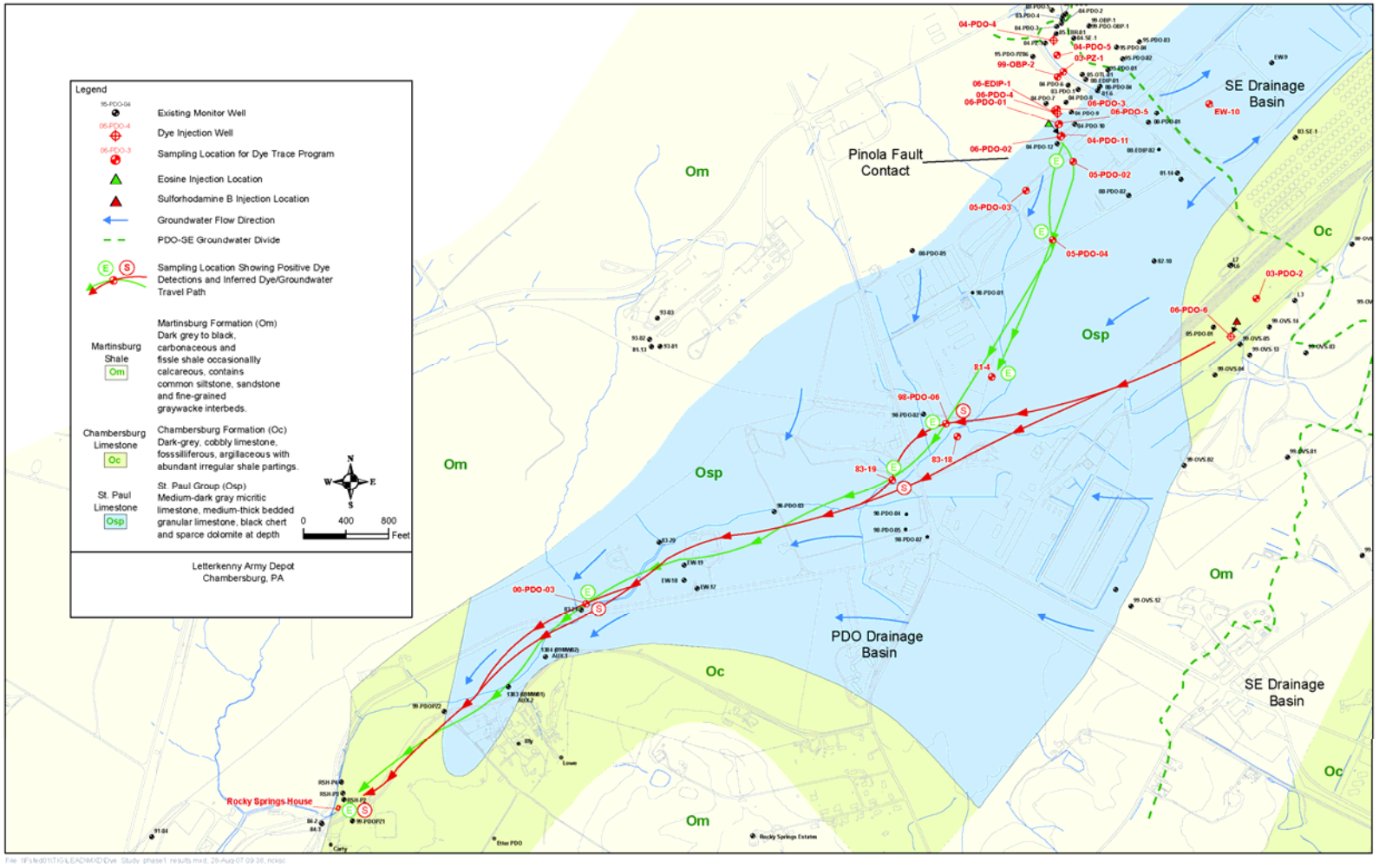

Figure 6. Results of the Phase I Portion of the Upper PDO Dye Tracing Program, 5 Dec 2006 to 22 Jan 2007

Table 1-A. Summary of Groundwater Velocities Based on Results from Phase I of the PDO Dye Trace Limestone to Limestone from Pinola Fault Area to Rocky Spring—Letterkenny Army Depot-Chambersburg, PA

Eosine Dye intro completed in well 04-PDO-11 @ 16:30 Hrs. on 12/5/06	**Distance From Intro Location (feet)**	**Date/Time of First Dye Arrival**		**Time From Dye Intro to Range of 1st Arrival (Hours)**		**Range of Groundwater Velocities**			
						feet/hour		**feet/day**	
Sampling Location		**Placed**	**Collected**	**Early**	**Late**	**High**	**Low**	**High**	**Low**
06-PDO-2U	5	ND	ND						
06-PDO-2L	5	ND	ND						
05-PDO-2	275	12/11/06 at 11:24	12/18/06 at 11:35	138.9	307.1	2.0	0.90	47.516	21.5
05-PDO-3	600	ND	ND						
05-PDO-4	1000	12/11/06 at 11:10	12/18/06 at 11:22	138.67	306.9	7.2	3.26	173.07	78.2
81-4	2350	12/27/06 at 10:40	1/9/07 at 11:26	522.34	834.9	4.5	2.81	107.98	67.5
98-PDO-6	2880	12/11/06 at 10:45	12/18/06 at 11:08	138.25	306.6	20.8	9.39	499.96	225.4
83-18	2950	ND	ND						
83-19	3560	12/8/06 at 08:20	12/11/06 at 10:18	63.84	137.8	55.8	25.83	1338.3	620.0
00-PDO-3	6610	12/18/06 at 10:43	12/27/06 at 10:04	306.22	521.6	21.6	12.67	518.06	304.2
RSH	9560	12/8/06 at 08:46	12/11/06 at 10:00	64.27	137.5	148.7	69.53	3569.9	1668.7

Table 1-B. Summary of Groundwater Velocities Based on Results from Phase I of the PDO Dye Trace Limestone to Limestone from Pad 5 Landfill Area to Rocky Spring—Letterkenny Army Depot-Chambersburg, PA

Sulforhodamine B Dye intro completed in well 06-PDO-6 @ 12:00 Hrs. on 12/5/06	**Distance From Intro Location (feet)**	**Date/Time of First Dye Arrival**		**Time From Dye Intro to Range of 1st Arrival (Hours)**		**Range of Groundwater Velocities**			
						feet/hour		**feet/day**	
Sampling Location		**Placed**	**Collected**	**Early**	**Late**	**High**	**Low**	**High**	**Low**
06-PDO-2U	N/A	ND	ND						
06-PDO-2L	N/A	ND	ND						
05-PDO-2	N/A	ND	ND						
05-PDO-3	N/A	ND	ND						
05-PDO-4	N/A	ND	ND						
81-4	2160	ND	ND						
98-PDO-6	2660	12/8/06 at 08:00	12/11/06 at 10:45	68	142.8	39.1	18.6	938.8	447.2
83-18	2620	ND	ND						
83-19	3310	12/7/06 at 08:55	12/8/06 at 08:20	44.92	68.33	73.7	48.4	1768.5	1162.6
00-PDO-3	6360	12/18/06 at 10:43	12/27/06 at 10:04	310.72	526.1	20.5	12.1	491.2	290.2
RSH	9310	12/8/06 at 08:46	12/11/06 at 10:00	68.76	142	135.4	65.6	3249.6	1573.5

ND-Indicates no dye detected at this location. **NA**-Not applicable; location far upgradient from dye intro point.

7. REFERENCES

Becher, A.E. and L.E. Taylor. 1982. *Groundwater Resources in the Cumberland and Contiguous Valleys of Franklin County, Pennsylvania.* Pennsylvania Geological Survey Water Resources Report 53. Harrisburg, PA.

Ozark Underground Laboratory (OUL). 1998. *Procedures and Criteria Analysis of Fluorescein, Eosine, Rhodamine WT, Sulforhodamine B, and Pyranine Dyes in Water and Charcoal Samplers.* February 1998.

Ozark Underground Laboratory (OUL). 2002. *Ozark Underground Laboratory's Groundwater Tracing Handbook.*

WESTON (Weston Solutions, Inc.). 2006. *Final Technical Plan for a Focused Dye Tracer Study of the Bedrock Aquifer in the Upper Property Disposal Office (PDO) Area of Letterkenny Army Depot, Chambersburg, PA.* September 2006.

WESTON (Weston Solutions, Inc.). 2004. *Remedial Investigation and Risk Assessment for the Building 37 Site (DSERTS Site LEAD-002), Southeastern Area (SE) Operable Unit (OU) 8. Letterkenny Army Depot, Chambersburg, PA.* Draft Report. April 2004.